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Microstructure Physics Group

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Research Activity

I. Syntheses and Structural Characterization of Zeolites and Mesoporous Materials

1. Electron Crystallography and Application for Structural Studies of Zeolite, Mesoporous Materials and Clusters in Zeolite.

(A. Carlsson, M. Kaneda, Y. Sakamoto, T. Ohsuna, N. Ohnishi, P. Wagner, K. Hiraga, R. Ryoo and O. Terasaki)

Micro- and mesoporous materials normally form as sub-micron sized crystals and as a result, the structure solution and refinement typically requires powder X-ray diffraction. Electrons interact with matter much more strongly than X-rays, so single crystal electron diffraction (ED) data-sets can be collected from sub-micron sized crystals. Because of their low density and absence of heavy atoms, we have confirmed kinematical scattering

approximation is effectively applicable for porous materials. Method for recovery of phase information of structure factors has been developed either from direct method analysis or from Fourier transform of high-resolution electron microscope images. The structure of unknown zeolite, SSZ-48, and structures of Fe oxide clusters in FAU have been solved by the former and later method, respectively. Only this method can solve the structure of mesoporous material, while other methods have been developed either for well-ordered (crystal) or for disordered (amorphous or liquid) materials.

2. Structures of Se-clusters in the Spaces of Zeolites, MOR and LTA

(N. Togashi, Y. Itoh, K. Sugiyama and O. Terasaki)

Se has an s^2p^4 valence configuration and takes either chain (trigonal Se) or crown-shape-ring structure(α-, β- and γ-Se). Three parameters, bond distance, bond and dihedral angles are important for the structure of Se-cluster. Sign of dihedral angle alternates around ring +-+- but stays constant along chain. Lone pair electrons play an important role for determining structures of clusters and their arrangement in crystals. The chain structure is a distortion of the simple cubic structure of Po, and reverts towards this structure under pressure. Se-clusters in zeolites are expected to take isolated ring or chain under the effects of (i) confinement in the spaces of zeolites and (ii) charge transfer between cluster and cation. Se-clusters are fully adsorbed in two different types of zeolites, Na-LTA (α-cages with diameter of ca 11.4Å) and Na-MOR (1-d channels with aperture of 6.5 x 7.0 Å). Their average structures are studied by X-ray diffraction (powder, single crystal, anomalous dispersion) and EM. Both systems keep the space group symmetries of original zeolites after incorporation of Se, they are Fm-3c for Se/Na-LTA and Cmcm for Se/Na-MOR. Se atoms are located on the three-fold and two-fold axes forming clusters in α-cages(ca. 13 Se-atoms per cage). By assuming bond angles are close to those of bulk crystal, Se_8 ring is most probable. Se-clusters are forming chains in the channel of MOR but the sequence of sign for dihedral angles are different from that of trigonal Se.

3. Structural Studies of New Mesoporous Materials and their Formation Mechanism.

(Y. Sakamoto, M. Kaneda, T. Ohsuna, K. Kuroda and O. Terasaki)

Mesoporous materials have pores that are much larger (say 30-100 Å) than those of zeolites. Using self organization of surfactant, they are synthesized from soluble silica or sheet silicate, e.g., Kanemite. The materials are periodic in terms of their pore arrangements and give fairly sharp diffraction peaks, while the wall are believed to be disordered and more closely resemble the structure of amorphous silica. Two formation mechanisms have been proposed, that is, liquid crystal templating and folded sheet mechanism. Starting from Kanemite, by intercalation and self-organization of surfactants, we succeeded in synthesizing new mesoporous material with lozenge shaped 1-d channels and observing structural change

from layered to mesoporous materials. This is the first definitive observation that folded sheet mechanism is operating.

4. Syntheses of New Microporous Materials and X-ray Structure Analyses

(J. Yu, N. Togashi, K. Sugiyama, K. Hiraga and O. Terasaki)

In order to make arrayed space especially with large spaces or 2-d character, it is very important to synthesize microporous materials with different structural moieties and leads to rational design. Aluminophosphates are interesting system, as we can change Al/P ratio from 1 to 2/3 by introducing terminal oxygen or OH bounded to the P atoms.

We have succeeded in synthesizing single crystals of many aluminophosphates and solving their structures. For example, 3-dimensionally connected microporous aluminophosphate AlPO-HAD (Al/P = 4/5) with interconnected 12- and 8-membered ring channel system which has not been observed in zeolites. Many layered types with Al/P =5/6, 4/5, 3/4 and 2/3 have been synthesized. We have also observed structural change from layer type to 3-d type by a condensation between successive layers upon heating, this might be a good sign for rational synthesis of porous materials.

II. Alkali Metal Clusters in Zeolite Cages

1. Metal-Insulator Transition of Potassium Clusters in Zeolite FAU

(Y. Ikemoto, T. Nakano and Y. Nozue)

Optical and magnetic properties are measured for K clusters generated in dehydrated zeolite K-form FAU with Si-to-Al ratio of 1.25. K clusters are found to be generated in the supercage of FAU. When K metal is adsorbed dilutely into K-FAU, an electron spin resonance (ESR) spectrum reveals that each cluster is isolated and in the insulator phase. From the analysis of the hyperfine structure of ESR spectrum, the cluster is assigned to K_3^{2+} in supercage. At higher loading density of K, 0.4 ± 0.1 atom per supercage, motional narrowing of the ESR spectrum is observed as well as the increase in the infrared absorption. These results indicate that the K clusters show insulator-to-metal phase transition. The effective magnetic moment per cluster is comparable to that expected from the number of the adsorbed K atoms. The observed insulator-to-metal transition is basically explained by the Mott transition.

2. Ferromagnetic and Paramagnetic Properties in Potassium Clusters Incorporated in Zeolite LTA

(T. Nakano, Y. Ikemoto, and Y. Nozue)

Magnetic and optical properties are investigated for potassium clusters incorporated in zeolite LTA at loading densities of K atoms between 3.5 and 7.2 per cluster, the latter of which is saturated. The Curie-Weiss law with negative Weiss temperature –35 K is seen at

3.5 atoms per cluster, and gradually approaches Curie law with increasing the loading density up to 7.2 atoms per cluster. The Curie temperature, ~8 K at 3.5 atoms per cluster, approaches zero Kelvin at 7.2 atoms per cluster. These results suggest that the antiferromagnetic coupling between localized magnetic moments of K clusters decreases with increasing K-loading density, and almost disappears at the K-loading density of 7.2 atoms per cluster. The insulator-like absorption tail is observed in the infrared region at any loading density, indicating that K clusters in LTA are in the Mott insulator phase. The average magnetic moment estimated from the saturation magnetization remarkably increases from 0.25 to 0.75 μ_B per cluster with increasing the loading density from 3.5 to 7.2 atoms per cluster. On the contrary , the average magnetic moment estimated from the Curie constant is ~1.6 μ_B per cluster, and almost independent of the loading density. It is not easy to explain these magnetic properties by the model of ferrimagnetism which was proposed in a previous paper (to be published in the European Physical Journal D).

3. Spin-Orbit Interaction in Alkali Metal Clusters

(Y. Nozue, Y. Ikemoto and T. Nakano)

A model of the enhancement effect on the spin-orbit interaction is proposed for alkali metal clusters, in order to explain the experimental results found in alkali metal clusters stabilized in zeolite cages, where the anomalous broadening of electron spin resonance spectrum and the remarkable decrease in the g-value are observed at higher loading densities of alkali metal. Ion cores of alkali atom are found to have a large enhancement effect on the spin-orbit interaction in the degenerated cluster orbital, such as the $1p$ state.

Master Theses

M1) Structure of Se-cluster confined in the space of LTA zeolite Yohei Itoh

M2) Optical Properties of Silicon Clathrate Compounds $Ba_8Ag_xSi_{46-x}$ Akira Kouno

Publications

1. Structural Characterisation of Micro- and Meso-porous Materials by Electron Microscopy
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12. Monoclinic $InPO_4$ $2H_2O$
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